OLIGOMERIZATION OF ISOPRENE

Kyoichi Suga and Syoji Watanabe

Translation of "Isoprene no oligomerization"
Kogyo Kogaku Zasshi, Vol. 69 pp 354-355, 1966

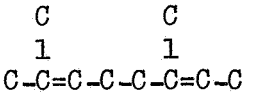
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON June 1968

OLIGOMERIZATION OF ISOPRENE

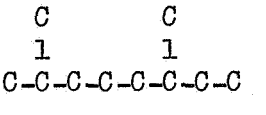
Kyoichi Sugan and Syoji Watanabe *

Various methods of oligomerization are known. For example, it is well known[1] that butadiene can be selectively dimerized using transition metal and organo aluminum compound. As a method of isoprene(I) dimerization, we have obtained dipentene[2] by acid or heating. Also, there are methods of isoprene dimerization I using aromatic hydrocarbon lithium compound and synthesized unsaturated compound.

The living polymer is widely utilized in anionic polymerization of I, styrene, and butadiene, but if the mole ratio of monomer is increased, the synthesis of oligomer with low degree of polymerization is theoretically possible. This experiment is conducted under this premise. I (1 mole) is added to a solution made from naphthalene*[2] (0.5 mole) in tetrahydrofuran and metalic lithium (2 mole). The reaction is stopped by methanol and obtained about 10-40% yield of dimer I (II). The composition is confirmed by analysis and existence of two double combinations was observed. The saturated compound obtained by hydrogenation of II was confirmed to be 2,6-dimethyl octane (III) by gas chromatography, infrared spectrum and nuclear magnetic resonance. Infrared spectrum of II shows absorption at 835 cm^{-1} and hydrogenated II shows absorption of gen-dimethyl group chain branching at 1380 cm^{-1}. This confirms the presence of isopyridine groups. Nuclear magnetic resonance of II shows two hydrogen atom $-\overset{|}{C}=CH$ signal near 4.87τ, four hydrogen atom $-\overset{|}{C}=CH_2$ signal near 8.05τ and twelve hydrogen atom signal near 8.40τ.



II



III

Signal near 8.40τ shows a complicated splitting and presumably indicates the presence of four methyl groups. When II is oxidized with potassium permanganate, acetic acid and acetone were generated. Above results suggest that the structure of II is 2,6-dimethyl 2,6-octadiene (II).

* Chemical Engineering, Chiba University, Syoseichyo Chibashi.

Examination of reaction conditions indicates that the yield of II is related to reaction temperature and maximum yield of 40% was obtained at 30°C. The best result was obtained when 0.5 mole of naphthalene is used for 1 mole of I. (Figs. 1 and 2). When metallic sodium and potassium were used in the experiment, II was not formed.

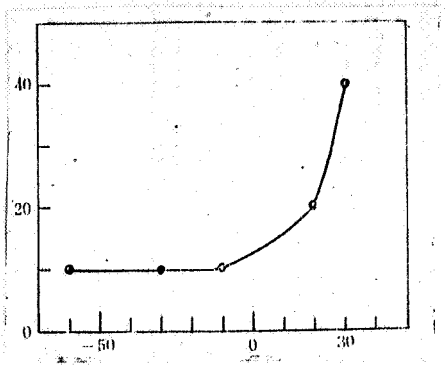


Fig. 1

1. Yield
2. Reaction temperature

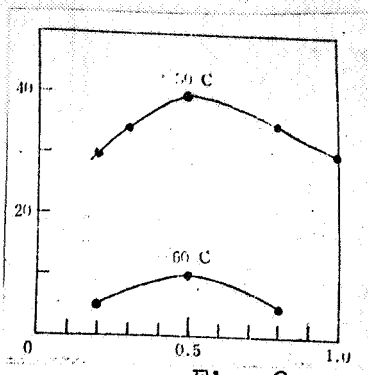


Fig. 2

1. Yield
2. Mol ratio (naphthalene/isoprene)

Experimental*3

40 g of I (0.54 mol) is added to a solution consisting of 40 g. naphthalene (0.312 mol), 8 g. of metallic lithium (1.15 mol) and 200 ml. of tetrahydrofuran and mixed for three hours. The reaction was stopped by adding methanol and the product was extracted with ether. After the usual treatment, 14 g*4 of II (bp_{40} 60-110°C) was obtained by distillation under reduced pressure. The purified material shows the following properties. bp_{85} 79-81°C, d_4^{20} 0.7777, n_D^{20} 1.4496, molecular refraction 47.77 (calculated value 47.44 based on C_{10} H_{18} F_2). Molecular weight (Rust method) 145 (calculated value 138 based on C_{10} H_{18}). Hydrogenation; Pd-C was used as catalyst and hydrogens corresponding to a double combination were absorbed. Infrared spectrum; 835 cm^{-1}, nuclear magnetic resonance; 4,87 τ (> = <, 2H), 8.05τ (=C - CH_2; 4H, triplet), 8,40τ(CH_3 group, 12H), Gas chromatography; single component. Analysis C 86.6%, H 13,07%

We would like to thank Dr. Hae Tanaka of the Mitsubishi company for the NMR measurement and his cooperation.

References

1. Saito, Ohno, Uchida and Goensei, Koka 66, 1099 (1963)
Ohtsuka, Takebu and Kikuchi, Koka 66, 1094 (1963)
2. Suga, Watanabe, 8th Meeting of Perfume, Terpene and Petroleum Chemistry. (1964)
3. Goenshyo, Uchida, Uchyo and Ohsawa; 18th Meeting of Japanese Chemistry. p. 445 (1965)

*2 Similar results are obtained with biphenyl, anthracene and freon.
*3 Reagent was thoroughly dried and purified. Reaction container was also dried and experiment was conducted in a netrogen atmosphere.
*4 Contains naphthalene and about 80% of II according to gas chromatography.

Received October 16, 1965